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*Published in:*  
Physical Review Letters

*DOI:*  
[10.1103/PhysRevLett.71.2469](https://doi.org/10.1103/PhysRevLett.71.2469)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1993

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Modesti, S., Cerasari, S., & Rudolf, P. (1993). Determination of Charge States of C60 Adsorbed on Metal Surfaces. *Physical Review Letters*, 71(15). <https://doi.org/10.1103/PhysRevLett.71.2469>

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## Determination of Charge States of $C_{60}$ Adsorbed on Metal Surfaces

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(Received 14 May 1993)

The charge transfer per molecule in a  $C_{60}$  monolayer on Au(110), on K/Au(110) $c(2\times 2)$ , and on a K multilayer has been determined by studying the electronic excitations from the valence bands and from the C 1s core level and the vibrational modes of the systems by electron energy loss spectroscopy. The electrons transferred are  $1\pm 1$ ,  $3\pm 1$ , and  $6\pm 1$ , respectively. These results indicate strong chemical bonding of  $C_{60}$  on such metal surfaces.

PACS numbers: 73.20.Dx, 79.20.Kz, 82.65.My

The physical properties, such as superconductivity, of  $C_{60}$  based compounds strongly depend on the number of electrons transferred to the carbon molecule [1]. This number in turn depends on the environment of the molecule. In vacuum, the neutral, singly, and doubly charged molecules are stable [2], in solid compounds  $C_{60}^{n-}$  anions ( $n\leq 10$ ) are stabilized by the Madelung potential [1,3], and in liquid solutions  $C_{60}^{n-}$  anions ( $n\leq 4$ ) are observed [4]. Theoretical calculations predict neutral, singly, and doubly charged states for molecules adsorbed on flat metal surfaces with decreasing work function, if chemical bonding with the substrate is excluded [5]. No calculations have been done taking into account bonding, and no experimental determination of charge transfer (CT) exists. The charge state of a  $C_{60}$  layer in contact with a metal plane is relevant to subjects like the dependence of superconductivity on dimensionality and geometry, or the physical properties of superlattices made by  $C_{60}$  and metals. By growing samples with triply charged  $C_{60}$  in different crystal structures the essential requirements for a superconductive state can be identified and studied.

We have determined the CT to a  $C_{60}$  monolayer (ML) from substrates with very different work functions and chemical reactivities, such as Au(110), K/Au(110) $c(2\times 2)$ , and a disordered K multilayer at 120 K. The CT has been estimated from the spectrum of the electronic excitations from the C 1s level to the empty  $C_{60}$  states, from the spectrum of the low-energy electronic excitations (0–8 eV), and from the energy shift of the dipole-active vibrational modes. We show that a ML of  $C_{60}$  on top of a metallic substrate can accept up to  $6\pm 1$  electrons per molecule.

99% pure  $C_{60}$  was sublimated from a Ta crucible at 750 K onto a clean Au(110)( $1\times 2$ ) surface. The coverage was determined from the ratio of the Au (69 eV) to C (270 eV) Auger peaks and calibrated from the ML coverage obtained by heating a  $C_{60}$  multilayer above 700 K [6]. A well-ordered quasihexagonal  $C_{60}$  ML on Au(110) [LEED pattern ( $6\times 5$ )] was produced by dosing with the substrate at 600 K as described in Ref. [6]. Well-ordered multilayers of  $C_{60}$  with (111) orientation

were obtained by dosing on top of an ordered ML at room temperature [6]. The K  $c(2\times 2)$  overlayer (0.5 K atom per Au surface atom) [7] was produced dosing K onto the Au substrate kept at 480 K and monitoring the LEED pattern as well as the ratio of the K (251 eV) to the Au (69 eV) Auger peak. The ordered  $C_{60}$  overlayer (hexagonal LEED pattern) on top of this substrate was achieved by dosing  $C_{60}$  at the same substrate temperature. Stable but disordered K multilayers were grown keeping the sample at 120 K [7]. On this substrate the  $C_{60}$  ML was dosed at 120 K and the absence of intermixing [8] was carefully checked by monitoring the coverage dependence of the intensities of the Auger peaks. The pressure during the measurements was  $4\times 10^{-11}$  mbar and it rose to  $2\times 10^{-9}$  mbar ( $6\times 10^{-10}$  mbar) during  $C_{60}$  (K) dosing.

The vibrational and low-energy electronic excitation spectra were collected with a high-resolution electron energy loss (HREEL) spectrometer (ELS 22). All spectra shown here were recorded in the specular geometry (electron incidence angle  $18^\circ$ ) with a primary electron energy of 2 eV (10 eV) and an energy resolution of 4–7 meV (15–20 meV) for the vibrational (electronic) excitation spectra. The dipole character of the excitation peaks was verified by recording also the off-specular spectra, which will be published elsewhere [9]. The C 1s absorption threshold was measured by electron energy loss spectroscopy (EELS) in the second-derivative mode with a cylindrical mirror analyzer. The primary electron energy was 400 eV and the peak-to-peak energy modulation 0.8 eV. The spectra relative to K multilayers were taken at 120 K; all the others at 300 K.

The electronic excitation spectrum of an ordered five layer  $C_{60}$  film is shown in Fig. 1. It is semiconductorlike, showing a gap of about 2 eV, sharp dipole-forbidden excitonic peaks in the range 1.5–2 eV, and band to band transition peaks at 2.2, 2.7, 3.0, 3.7, 4.4, and 6.7 eV, in agreement with previously published data [10]. On the contrary, the excitation spectrum of a monolayer of  $C_{60}$  on Au(110) (Fig. 1) is metalliclike, without any excitonic structure, but with a continuum of transitions in the gap of solid  $C_{60}$  which is peaked at 0.9 eV. If a gap exists, it

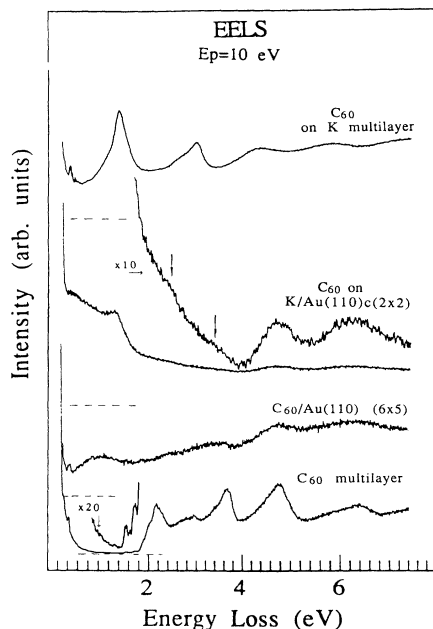


FIG. 1. EEL spectra of bulk  $C_{60}$  and of  $C_{60}$  monolayers on different substrates. The dashed line under each spectrum marks the zero level. The broad feature below 1 eV in the second and third spectra is the  $t_{1u}$  plasmon.

is masked by the vibrational excitations of  $C_{60}$  (sharp peaks below 200 meV) and of CH containing contaminants (360 meV). The other structures of the spectrum are much broader than the corresponding ones of solid  $C_{60}$  and slightly displaced in energy.

In a ML of  $C_{60}$  on a  $K/Au(110)c(2 \times 2)$  substrate the lowest-energy structure grows in intensity and transforms into a smooth background centered at about 0.5 eV, while a new strong peak at 1.3 eV develops (Fig. 1). This energy differs less than 0.1 eV from that of the second structure of the EEL spectrum of  $K_3C_{60}$  [11] and  $Rb_3C_{60}$  [12]. The first structure of  $K_3C_{60}$  and  $Rb_3C_{60}$  at 0.55 eV is broadened in the adsorbed layer. The other structures in the spectrum, two weak shoulders at 2.4 and 3.4 eV (see arrows) and two peaks at 4.6 and 6.3 eV, have energies which are within 0.2 eV of those of the corresponding features in  $K_3C_{60}$ . In a ML of  $C_{60}$  on top of two disordered layers of K on Au(110) the excitations below 1 eV have disappeared, and the main structures are now at 1.35, 2.6, 3.0, 4.3, and 5.8 eV. The first peak is at exactly the same energy as the corresponding one measured for  $K_6C_{60}$  [11],  $Rb_6C_{60}$  [12], and  $Ca_3C_{60}$  [3]; all the other excitations differ by less than 0.1 eV from those of  $K_6C_{60}$ . The main low-energy structures in the spectra of Fig. 1 correspond to excitations in the  $C_{60}$  layers because the substrates give contributions at different energies or with much larger linewidth. In fact, the spectrum of Au shows broad peaks at 2.8, 4, and 6 eV, that of  $K/Au(110)c(2 \times 2)$  has a strong peak at 1.3 eV with a full width at half maximum (FWHM) larger than 2.5 eV,

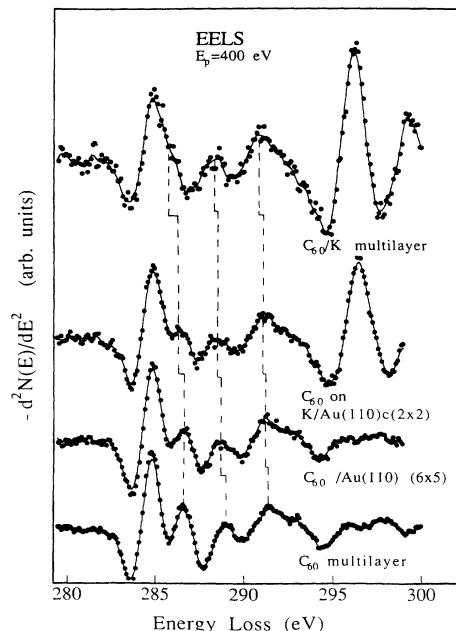


FIG. 2. Second derivative of the EEL spectra of the C 1s absorption edge of bulk  $C_{60}$  and of  $C_{60}$  monolayers on metallic substrates. The peaks at 296 and 299 eV are the K  $L_{23}$  edges.

and that of a K double layer has a surface plasmon at 2.2 eV (1.5 eV FWHM) and a "bulk" plasmon at 3.8 eV [9].

Let us focus now on the lowest-energy excitations, i.e., those that show the highest environment sensitivity. In  $K_3C_{60}$  (charge state  $C_{60}^{3-}$ ) the 0.55 eV peak is the plasmon associated to the three extra electrons per molecule which half fill the lowest unoccupied molecular orbital (LUMO)  $t_{1u}$  band [11] (the plasmon is broadened and shifted by degenerate intraband and interband transitions), while the 1.3 eV peak corresponds to dipole-allowed transitions from the LUMO  $t_{1u}$  to the  $t_{1g}$  level. In  $K_6C_{60}$ ,  $Rb_6C_{60}$ , and  $Ca_3C_{60}$  (charge state  $C_{60}^{6-}$ ) the  $t_{1u}$  level is filled and therefore the 0.55  $t_{1u}$  plasmon vanishes and only the interband  $t_{1u}-t_{1g}$  transitions at 1.3 eV survive [3,11,12].

The presence of the  $t_{1u}$  plasmon in the  $C_{60}$  ML on Au(110) indicates that the  $t_{1u}$  level begins to fill in this system. The similarity between the spectra of  $C_{60}$  on  $K/Au(110)c(2 \times 2)$  and of  $K_3C_{60}$  and the intensity of the  $t_{1u}$  plasmon, comparable to that of the 1.3 eV peak as in  $K_3C_{60}$ , show that the LUMO is roughly half filled in this case. The absence of the  $t_{1u}$  plasmon in  $C_{60}$  on the K multilayer and the strong similarity of the spectrum of this system with that of  $K_6C_{60}$  indicate that the sixfold degenerate LUMO is essentially filled on a K surface.

This conclusion is quantitatively confirmed by the study of the empty  $C_{60}$  levels by means of the C 1s core level excitation spectra. Figure 2 shows the second derivative of the C 1s absorption edge measured by EELS. The peaks at 284.8, 286.7, 288.9, 291.4, 293, 295.9, and 297.8 eV in the spectrum of a five layer  $C_{60}$

film are in good agreement with the maxima of the absorption coefficient measured in bulk  $C_{60}$  [11,13,14]. The first three peaks are transitions to the  $t_{1u}$ , to the  $(t_{1g} + t_{2u} + h_g)$ , and to the  $(g_u + g_g + t_{2g})$  levels, respectively.

The third and fourth peaks shift to lower energy by about 0.2 eV in a ML of  $C_{60}$  on Au(110), by about 0.35 eV, together with the second peak, on K/Au(110)c(2×2), and by about 0.8 eV in a ML of  $C_{60}$  on a two layer K film. The peaks at 296 and 299 eV are the K 2p-3d excitations. These shifts, similar to those observed on going from  $C_{60}$  to  $K_3C_{60}$  (−0.5 eV) and to  $K_6C_6$  [11,14] and  $Ca_3C_{60}$  (−0.9 eV) [3], reflect the filling of the  $t_{1u}$  level and the lowering of the other empty states with respect to the Fermi level. The first peak in the  $K_6C_{60}$  spectrum [14] and in the top spectrum in Fig. 2 is due to transitions at the new LUMO  $t_{1g}$  level. Assuming a linear relationship between the energy shifts and CT (−0.15 eV/electron from the published bulk data), and an experimental error of 0.1 eV in our data, a CT of  $1.3 \pm 0.7$ ,  $2.3 \pm 0.7$ , and  $5.3 \pm 0.7$  electrons is obtained for the three substrates.

An additional quantitative confirmation of the considerable CT to the adsorbed  $C_{60}$  molecules comes from the large energy shift of the molecular vibrational modes. The bottom curve in Fig. 3 shows the HREEL spectrum of a 5 ML  $C_{60}$  film. The main peaks at 66, 146, and 178 meV and the shoulder at 72 meV are the four dipole-active  $t_{1u}$  modes [15,16]. The lowest-energy  $t_{1u}$  mode is strongly attenuated with respect to the others and shifts

by 3 meV when the molecules are adsorbed on Au(110), by 6 meV when they are adsorbed on K/Au(110)c(2×2), and by 7 meV on a K double layer. The energies of the second and third  $t_{1u}$  modes, at 72 and 146 meV, respectively, are not appreciably affected by adsorption, but the relative intensity of the second  $t_{1u}$  mode increases. On the contrary, the highest-energy  $t_{1u}$  mode shows the strongest substrate dependence: It shifts from 178 meV for a  $C_{60}$  multilayer and 1 ML  $C_{60}$  on Au(110) to 175 meV for 1 ML  $C_{60}$  on K/Au(110)c(2×2), and to 165 meV for 1 ML  $C_{60}$  on a K double layer or multilayer, steadily growing in relative intensity. This behavior is again strikingly similar to what has been observed for alkali-doped  $C_{60}$  [15]. In fact, in  $K_6C_{60}$  the first and the fourth  $t_{1u}$  modes shift by 7 and 11 meV, respectively, with respect to bulk  $C_{60}$ , while the energies of the other two modes are scarcely affected by the CT. The similarity also extends to the substrate dependence of the intensities of the second and the fourth  $t_{1u}$  modes, which are enhanced by nearly 2 orders of magnitude by alkali doping both in bulk compounds [15] and in our systems.

Theoretical calculation [17] shows that the coupling to virtual  $t_{1u}$ - $t_{1g}$  electronic transitions causes a linear dependence of the energy shifts of the  $t_{1u}$  modes on the number of transferred  $t_{1u}$  electrons (by −1.8 meV per electron for the 178 meV mode), while the intensities have a quadratic dependence. *Ab initio* molecular dynamics calculations [18] predict different charge transfer shifts for the four  $t_{1u}$  modes, in agreement with our results: Only the first and fourth modes show negative energy shifts (−4 meV) in a  $Li_{12}C_{60}$  cluster, where twelve extra electrons are added to  $C_{60}$  [18].

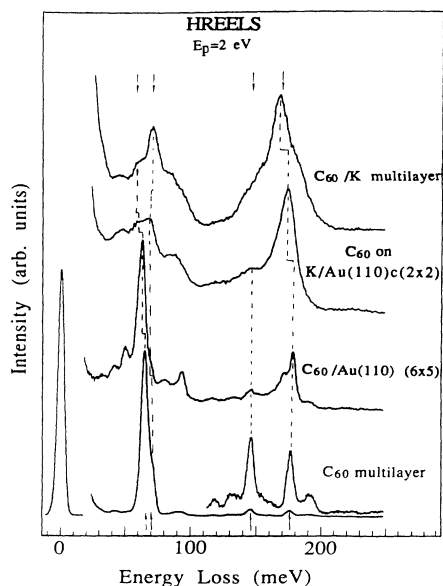


FIG. 3. HREEL vibrational spectra of bulk  $C_{60}$  ( $\times 50$  and  $\times 500$ ) and of  $C_{60}$  monolayers on Au(110) ( $\times 300$ ), K/Au(110) ( $\times 350$ ), and K multilayer ( $\times 50$ ), measured in the specular geometry. The arrows at the bottom indicate the energies of the dipole-active  $t_{1u}$  modes in bulk  $C_{60}$ , and those on top indicate the energies of the corresponding modes in bulk  $K_6C_{60}$ .

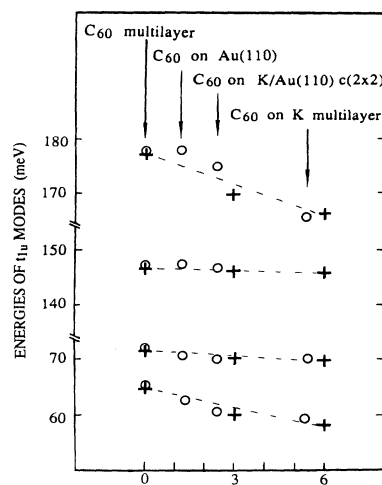


FIG. 4. Energies of the four  $t_{1u}$  vibrational modes of  $C_{60}$  on different metallic substrates (circles). The dashed lines connect the points corresponding to  $t_{1u}$  modes in bulk  $C_{60}$  (crosses at left) and bulk  $K_3C_{60}$  (crosses at the right) [15]. The data of  $K_3C_{60}$  are also reported (crosses at the center) [19].

The measured energies of the  $t_{1u}$  modes of bulk  $C_{60}$  [15],  $K_3C_{60}$  [19], and  $K_6C_{60}$  [15] are reported in Fig. 4 as a function of CT (crosses). The energy shifts in the bulk compounds, nearly linear with respect to CT, are  $-1.25$  meV/electron and  $-1.8$  meV/electron for the first and fourth modes, respectively. Our data for adsorbed  $C_{60}$  layers are also reported in Fig. 4 (circles) as a function of the CT estimated from the spectra of Figs. 1 and 2. The energies are obtained by least-squares fitting of the vibrational spectra with Gaussian peaks and the error bar is  $\pm 0.5$  meV [9]. The data points fall close to the line which fits the bulk data. An independent estimate of the charge transfer can be made from the energies of the first and fourth modes by using the above mentioned energy shifts in the bulk compounds as a calibration. The number of transferred electrons calculated this way is 0, 1.7, and 6.7 for  $C_{60}$  on Au(110), on K/Au(110) $c(2\times 2)$ , and on the K multilayer, respectively, if the fourth mode is used, and 2.3, 4.4, and 5.6 transferred electrons for the same systems if the first mode is used. The error bar is  $\pm 0.7$  electron in both cases. These values are in good agreement with those estimated from the data of Figs. 1 and 2. The discrepancies in the numbers obtained from the two modes are due to some nonlinearity in the shifts, probably caused by the distortion of the molecules due to the bonding to the substrate. However, the averages of the values given by the two modes, 1.2, 3.1, and 6.2 electrons for the three systems, are fully consistent with the estimations based on the electronic excitations. We can safely conclude that the CT is between 0 and 2 electrons on Au(110), between 2 and 4 electrons on K/Au(110) $c(2\times 2)$ , and between 5 and 7 electrons on K films.

On Au(110), every  $C_{60}$  molecule is in close contact with two Au ridge atoms of the  $(1\times 5)$  reconstructed surface [6]. These atoms have only seven nearest neighbor Au atoms, i.e., 42% less than bulk atoms. Therefore roughly half an electron per ridge atom is available for bonding to  $C_{60}$ . This quantity agrees with the above estimated CT. We expect that the CT would be appreciably lower on less open and less reactive Au surfaces such as (111) and (100). Theoretical estimates [5] predict a CT substantially less than 1 electron on flat Au surfaces, because of the high work function (5.4 eV). For a  $C_{60}$  ML (surface density  $n_s = 1.1 \times 10^{14}$  cm $^{-2}$ ) on K/Au(110) $c(2\times 2)$  ( $n_s = 4.2 \times 10^{14}$  cm $^{-2}$ ), there are 3.8 potassium atoms per  $C_{60}$  molecule, while on a K multilayer there are 5 K surface atoms per  $C_{60}$  molecule [ $n_s = 5.6 \times 10^{14}$  cm $^{-2}$  for a K(111) surface]. Therefore more than half of the K electronic charge available for bonding is transferred to the  $C_{60}$  overlayer on the  $c(2\times 2)$

K layer. On a potassium multilayer the charge transferred is at least the entire amount available for bonding in the top K layer. The work functions of a ML and of a multilayer K film are the same (2.3 eV) within less than 0.2 eV [9]. Therefore the effect of a work function change is not significant and we attribute the difference in the number of transferred electrons to the competing effect of bond formation between K and Au which sensibly decreases the electron density in the vacuum side of an alkali ML [20]. An additional contribution to CT in the multilayer could come from surface disorder [5].

In conclusion, we have shown that the charge state of a  $C_{60}$  layer on a metallic surface can be varied in a wide range (up to 6 electrons per molecule) by choosing an appropriate substrate and can be consistently measured by the vibrational and electronic excitations spectra.

We wish to thank E. Tosatti and W. Andreoni for helpful discussions.

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